## PATENT COOPERATION TREATY





#### INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SJW/7096-PCT	FOR FURTHER see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.				
International application No.	International filing date (day/month/year)	(Earliest) Priority Date (day/month/year)			
PCT/EP 00/06016	28/06/2000	08/07/1999			
Applicant CERESTAR HOLDING B.V.					
This International Search Report has bee according to Article 18. A copy is being tr	en prepared by this International Searching Auransmitted to the International Bureau.	thority and is transmitted to the applicant			
	s of a total of3 sheets. v a copy of each prior art document cited in this	s report.			
	international search was carried out on the ba less otherwise indicated under this item.	isis of the international application in the			
the international search v Authority (Rule 23.1(b)).	vas carried out on the basis of a translation of	the international application furnished to this			
was carried out on the basis of th  contained in the internation  filed together with the internation  furnished subsequently to  the statement that the subsequently to the statement that the subsequently to the statement that the infernational application at the statement that the infernation at the statement that the infernation at the statement that the infernation at the statement that the statement that the infernation at the statement that the statement that the infernation at the statement that the statement that the statemen	ne sequence listing:  conal application in written form.  ernational application in computer readable for  this Authority in written form.  this Authority in computer readble form.  beguently furnished written sequence listing of  as filed has been furnished.  ormation recorded in computer readable form				
	ind unsearchable (See Box I).				
4. With regard to the title,  The text is approved as su	ubmitted by the applicant. Shed by this Authority to read as follows:				
the text has been establis	ubmitted by the applicant. shed, according to Rule 38.2(b), by this Author e date of mailing of this international search re				
6. The figure of the <b>drawings</b> to be pub  as suggested by the appl because the applicant fail because this figure better	icant.	None of the figures.			

International Application No

PCT/EP 00/06016 A. CLASSIFICATION OF SUBJECT M IPC 7 A23G3/00 3G3/02 A23G3/30 A23L1/25 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) A23G A23L Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, FSTA C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Category 6 Relevant to claim No. Υ FRITZSCHING, B.: "Isomalt in hard candy 1,5-8applications." MANUFACTURING CONFECTIONER., vol. 75, no. 11, 1995, pages 65-73, XP000862872 CHICAGO, IL., US ISSN: 0163-4364 cited in the application page 67, column 2 -column 3 page 69, column 1 page 70, column 1 -page 71, column 3; figure 7 figure 8 Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the "O" document referring to an oral disclosure, use, exhibition or document is combined with one or more other such do ments, such combination being obvious to a person skilled document published prior to the international filing date but later than the priority date claimed in the art. "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 9 November 2000 17/11/2000 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Heezius, A Fax: (+31-70) 340-3016

International Application No PCT/EP 00/06016

	Lation) DOCUMENTS CON ED TO BE RELEVANT	los services
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RALEIGH W: "HSH as a bulking agent in confections."  MANUFACTURING CONFECTIONER., vol. 75, no. 11, 1995, pages 57-59, XP000957699  CHICAGO, IL., US ISSN: 0163-4364 page 57, right-hand column, paragraph 3 -page 58, right-hand column, paragraph 2 page 58, right-hand column, paragraph 2 -page 59, left-hand column, paragraph 4; figure 3	1,5-8
Α	DE 42 28 278 A (SIGRIST, E.) 20 January 1994 (1994-01-20) cited in the application column 1, line 66 -column 2, line 28; claims 1-3	1,3
Α	EP 0 788 744 A (LOTTE CO. LTD) 13 August 1997 (1997-08-13) cited in the application page 3, line 25 - line 31; claims 9-11; example 8	1,3
Α	EP 0 500 977 A (ZOSTER, S.A.) 2 September 1992 (1992-09-02) cited in the application example 4	1,3
Α	US 5 578 339 A (KUNZ ET AL.) 26 November 1996 (1996-11-26) claims 1-6,21,22	1,3
Α	HÖRLEIN L.: "Production of low-calorie strawberry jam pleasant in taste and suitable for diabetics using both acesulfame-K and aspartame."  INDUSTRIELLE OBST- UND GEMUESEVERWERTUNG, vol. 80, no. 1, 1995, page 2-7 XP000863024 WOLFSBURG, DE ISSN: 0367-939X page 3, column 1	1,3
Α	EP 0 390 299 A (TOWA CHEMICAL INDUSTRY CO. LTD.) 3 October 1990 (1990-10-03) page 3, line 31 - line 40 page 3, line 52 - line 53	1,3
A	EP 0 504 924 A (HOECHST AKTIENGESELLSCHAFT) 23 September 1992 (1992-09-23) column 2, line 15 - line 28; claims 1-4,8,10	1-9

Information on patent family members

International Application No
PCT/EP 00/06016

Patent document cited in search repo	rt	Publication date		Patent famil member(s)		Publication date
DE 4228278	A	20-01-1994	СН	684148	Α	29-07-1994
DE 1220270	^,	20 01 1994	FR	2693631		21-01-1994
			NL	9301254		16-02-1994
						10 02 1994
EP 788744	Α	13-08-1997	JP	9252723		30-09-1997
			AU	1019297		24-07-1997
	•		BR	9700121		22-09-1998
			CA	2195350		19-07-1997
			CZ	9700153		13-08-1997
			HU	9700164		28-10-1997
			NZ	314082		26-05-1997
			PL	318004		21-07-1997
			RU	2142711		20-12-1999
			US	5711982	Α	27-01-1998
EP 500977	A	02-09-1992	DE	69111050	D	10-08-1995
			DE	69111050		23-11-1995
			US	5300309		05-04-1994
US 5578339	Α	26-11-1996	AT	140032	T	<del></del> 15-07-1996
			AU	666073		25-01-1996
			AU	6194094		10-11-1994
			DE	9321600		06-04-2000
			DE	59303142		08-08-1996
			DK	625578		11-11-1996
		•	EP	0625578		23-11-1994
		٠,	ES	2089691		01-10-1996
			GR	3020742		30-11-1996
			IL	109569		10-03-1998
			JP	7051079		28-02-1995
 EP 390299	Α	03-10-1990	AT	91389	 Т	15-07-1993
	* *	<del>-</del> <del>-</del>	DE	69002177		19-08-1993
			DE	69002177		28-10-1993
			JP	2257848		18-10-1990
				2000078954		21-03-2000
 EP 504924		23-09-1992	CA	2063645	 А	23-09-1992
· <del> ·</del>	- •		JP	5262782		12-10-1993



### From the INTERNATIONAL SEARCHING AUTHORITY

STEVENS HEWLETT & PERKINS Attn. WILKINSON, Stephen John 1 St. Augustine's Place

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

Bristol BS1 4UD UNITED KINGDOM	(PCT Rule 44.1)				
	•				
	Date of mailing (day/month/year) 17/11/2000				
Applicant's or agent's file reference					
SJW/7096-PCT	FOR FURTHER ACTION See paragraphs 1 and 4 below				
International application No. PCT/EP 00/06016	International filing date (day/month/year) 28/06/2000				
Applicant					
CERESTAR HOLDING B.V.					
1. X The applicant is hereby notified that the International Search Filing of amendments and statement under Article 19:					
The applicant is entitled, if he so wishes, to amend the claim	ns of the International Application (see Rule 46):				
When? The time limit for filing such amendments is normal International Search Report; however, for more de	ally 2 months from the date of transmittal of the tails, see the notes on the accompanying sheet.				
Where? Directly to the International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Fascimile No.: (41–22) 740.14.35	;				
For more detailed instructions, see the notes on the accompanying sheet.					
2. The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.					
3. With regard to the protest against payment of (an) addition	nal fee(s) under Rule 40.2, the applicant is notified that:				
the protest together with the decision thereon has been applicant's request to forward the texts of both the protest.	n transmitted to the International Bureau together with the test and the decision thereon to the designated Offices.				
no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.					
4. Further action(s): The applicant is reminded of the following:					
Shortly after <b>18 months</b> from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90 <i>bis</i> .1 and 90 <i>bis</i> .3, respectively, before the completion of the technical preparations for international publication.					
Within 19 months from the priority date, a demand for international wishes to postpone the entry into the national phase until 30 mo					
Within 20 months from the priority date, the applicant must perfor before all designated Offices which have not been elected in the priority date or could not be elected because they are not bound	e demand or in a later election within 19 months from the				

Name and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2

NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

Authorized officer

Emmanuel Cherqui

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

#### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international polication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been lis filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

#### What documents must/may accompany the amendments?

#### Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

## The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

- 1. [Where originally there were 48 claims and after amendment of some claims there are 51]: "Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
- [Where originally there were 15 claims and after amendment of all claims there are 11]:
   "Claims 1 to 15 replaced by amended claims 1 to 11."
- [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
   "Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
   "Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
- 4. [Where various kinds of amendments are made]: "Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

#### "Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

#### It must be in the language in which the international appplication is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

#### Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

#### Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

Intern val Application No PCT/EP 00/06016

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A23G3/00 A23G3/02

3G3/02 A23G3/30

A23L1/236

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 A23G A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, FSTA

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Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Υ .	FRITZSCHING, B.: "Isomalt in hard candy applications." MANUFACTURING CONFECTIONER., vol. 75, no. 11, 1995, pages 65-73, XP000862872 CHICAGO, IL., US ISSN: 0163-4364 cited in the application page 67, column 2 -column 3 page 69, column 1 page 70, column 1 -page 71, column 3; figure 7 figure 8	1,5-8

X Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
<ul> <li>Special categories of cited documents:</li> <li>"A" document defining the general state of the art which is not considered to be of particular relevance</li> <li>"E" earlier document but published on or after the international filling date</li> <li>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the priority date claimed</li> </ul>	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
9 November 2000	17/11/2000
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Heezius, A

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intern: al Application No PCT/EP 00/06016

Patent document cited in search report		Publication dat		Patent family member(s)	Publication dat
DE 4228278	_A	20-01-1994	CH FR	684148 A 2693631 A	29-07-1994 21-01-1994
			NL	9301254 A	16-02-1994
EP 788744	A	13-08-1997	JP	9252723 A	30-09-1997
			AU	1019297 A	24-07-1997 22-09-1998
			BR	9700121 A 2195350 A	19-07-1997
			CA CZ	9700153 A	13-08-1997
			HU	9700153 A 9700164 A	28-10-1997
			NZ	314082 A	26-05-1997
			PL	318004 A	21-07-1997
			ŔŨ	2142711 C	20-12-1999
			US	5711982 A	27-01-1998
EP 500977		02-09-1992	DE	69111050 D	10-08-1995
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	<b>.</b>		<b>€</b> US	53003 <del>09 A</del>	05-04-1994
US 5578339	A	26-11-1996	AT	140032 T	15-07-1996
			AU	666073 B	25-01-1996
			AU	6194094 A	10-11-1994 06-04-2000
			DE De	9321600 U 59303142 D	08-08-1996
			DK	625578 T	11-11-1996
			EP	0625578 A	23-11-1994
			ĒS	2089691 T	01-10-1996
			GR	3020742 T	30-11-1996
			IL	109569 A	10-03-1998
		_	JP	7051079 A	28-02-1995
EP 390299	Α	03-10-1990	AT	91389 T	15-07-1993
<u></u>			DE	69002177 D	19-08-1993
			DE	69002177 T	28-10-1993
			JP	2257848 A	18-10-1990
			JP :	2000078954 A	21-03-2000
EP 504924	Α	23-09-1992	CA	2063645 A	23-09-1992
			JP	5262782 A	12-10-1993





PCT

#### NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

WILKINSON, Stephen, John Stevens, Hewlett & Perkins 1 St. Augustine's Place Bristol BS1 4UD ROYAUME-UNI

Date of mailing (day/month/year) 15 September 2000 (15.09.00)	
Applicant's or agent's file reference SJW/7096-PCT	IMPORTANT NOTIFICATION
International application No. PCT/EP00/06016	International filing date (day/month/year) 28 June 2000 (28.06.00)
International publication date (day/month/year)  Not yet published	Priority date (day/month/year) 08 July 1999 (08.07.99)

CERESTAR HOLDING B.V. et al

- 1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- 2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- 3. An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- 4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an apportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date Priority application No.

Country or regional Office or PCT receiving Office of priority document

O8 July 1999 (08.07.99)

9915883.4

GB

10 Augu 2000 (10.08.00)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer

Catherine Massetti

Telephone No. (41-22) 338.83.38

Facsimile No. (41-22) 740.14.35

## From the INTERNATIONAL BUREAU

NOTICE INFORMING THE APPLICANT OF THE **COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES** 

(PCT Rule 47.1(c), first sentence)

To: WILKINSON, Stephen, John Stevens, Hewlett & Perkiller 1 St. Augustine's Place KINS Bristd BS1 4UDBRISTOL ROYAUME-UNI 29 JAN 2001 DIA 四川段 IMPORTANT NOTICE

Date of mailing (day/month/year)

18 January 2001 (18.01.01)

Applicant's or agent's file reference

SJW/7096-PCT

International application No. PCT/EP00/06016

International filing date (day/month/year) 28 June 2000 (28.06.00)

Priority date (day/month/year) 08 July 1999 (08.07.99)

**Applicant** 

CERESTAR HOLDING B.V. et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice: AG, AU, DZ, KP, KR, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD, GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX, NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 18 January 2001 (18.01.01) under No. WO 01/03513

#### REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

#### REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer

J. Zahra

Telephone No. (41-22) 338.83.38

Facsimile No. (41-22) 740.14.35

#### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

## (19) World Intellectual Property Organization International Bureau



## 

## (43) International Publication Date 18 January 2001 (18.01.2001)

#### **PCT**

# (10) International Publication Number WO 01/03513 A1

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(54) Title: PREPARATION OF SUGAR-FREE HARD CANDY

(57) Abstract: The present invention discloses a syrup at dry substance between 60 % to 80 % consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup wherein the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22 % w/w and 55 % w/w higher polyols, preferably between 25 % w/w and 50 % w/w higher polyols. Non-sticky, non-hygroscopic and non-cariogenic sugar-free hard candies comprising aforementioned syrup and the corresponding process are disclosed.

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#### Preparation of Sugar-free Hard candy

#### Technical field

The present invention relates to mixtures consisting of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup. The dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols. The present invention also discloses a process for producing sugar-free hard candies. In addition, a new type of sugar-free hard candies is disclosed. The candies are non-hygroscopic, non-sticky, non-cariogenic and show excellent mass viscosity.

#### Background of the invention

Recent developments in hard candy manufacture have been the replacement of part or all of the sugar by a sugar alcohol (polyol) in the interest of providing a product having a reduced calorie content and a lower tendency to cause tooth decay. Among the polyols, which have been proposed for the manufacture of hard candy, are isomalt, maltitol, xylitol, erythritol and others.

EP 0 533 334 describes a process for the production of hard candy characterised in that the maltitol content of the sugar alcohol mixture is more than 77% but less than 86% by weight based on dry substance. When the mixture contains 77% or less maltitol the resultant candies become increasingly hygroscopic and sticky, while when the mixture contains 86% and higher maltitol the candies rapidly become opaque as a result of the maltitol crystallisation.

EP 0 611 527 describes a controlled propagation of crystallisation of maltitol in hard candies by applying molecules of molecular weight greater than 1,300 Dalton, preferably greater than 2,000 Dalton and more preferably greater than 3,000 Dalton. Preferably syrups comprising more than 78% maltitol are applied, since syrups comprising less than 60% maltitol give unsatisfactory results in respect to hygroscopicity, cariogenicity and unsuitable application.

US 4,971,798 describes a hydrogenated isomaltulose based hard confection which contains, in addition to the hydrogenated isomaltulose, a medicinal active ingredient. Such a formulation has been found to dissolve more slowly than similar formulations

based on sugar, rendering them suitable for dispensing the active ingredient over an extended period time.

Furthermore, it is common general knowledge that hard candies based on hydrogenated isomaltulose are non-hygroscopic but the mass viscosity of hard candies based on hydrogenated isomaltulose is low.

WO 97/30598 describes a sweetener consisting of especially 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS) and 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM), and the use of this sweetener in hard and soft caramels, especially pharmaceutically active caramels. The presence of 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS) results in candies with improved solubility, higher sweetness and lower ability to crystallise, but hard candies based on these hydrogenated isomerised saccharose syrups have even lower mass viscosity than the hard candies based on hydrogenated isomaltulose.

Fritzsching, in The Manufacturing Confectioner Vol 75, No. 11, 1995, pages 65 – 73, describes isomalt in hard candy applications. He demonstrates that the hard candies prepared with 80% isomalt and 20% of a hygroscopic polyol have a higher hygroscopicity than hard candies prepared with pure isomalt. If isomalt is blended with hygroscopic polyols or bulking agents a more excessive packaging like twist wrapping is required. Due to their slight stickiness, loose packing in boxes is not possible.

DE 4228278 discloses a fondant and its production process. The sugar-free fondant comprises 75 to 90% w/w disaccharide alcohol and 10 to 25% w/w of water. The fondant is used in particular as icing agent, and for fillings of pralines. The disaccharide alcohol can be isomalt, maltitol and the like.

EP 0500977 relates to body and mouthfeel potentiated foods and beverages containing neohesperidin dihydrochalcone and a process for preparing them. It describes the flavour and sweetness profile when applying neohesperidin dihydrochalcone.

EP 0788744 relates to de-lactose milk and de-lactose milk powder which are reconstructed with milk proteins and milk fats as major components free or almost free of lactose. Furthermore, the invention relates to foodstuffs containing de-lactose milk and/or de-lactose milk powder. When the de-lactose milk and the de-lactose milk powder are

used for the sugar-less foodstuffs, one or more sugar alcohols selected from the group consisting of lactitol, palatinit and maltitol may preferably be used as a sweetener.

A process for producing hard candies comprises preparation of syrups, cooking at elevated temperature and shaping including a cooling phase. The mass viscosity of the hot (temperature > 90°C) syrups is determining the workability and the processing time of the cooling phase. Applying low viscous syrups results during the cooling phase of the shaping of hard candies in a very liquid mass, which needs a considerably long processing time before the mass can be shaped in moulds.

Accordingly, there is a need for highly viscous syrups which are non-hygroscopic and which can be used for the preparation of i.e. sugar-free non-hygroscopic, non-sticky and non-cariogenic hard candies. Applying high viscous syrups shortens the processing time of the cooling phase considerably and it results in an economical advantageous process.

#### Summary of the invention

The present invention discloses a syrup at dry substance between 60% to 80%, preferably at dry substance of about 70% consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup characterised in that the dry substance of the syrup comprises 86% w/w isomalt, preferably between 85% w/w and 79% w/w isomalt, more preferably 75% w/w isomalt, and the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols, preferably between 25% w/w and 50% w/w higher polyols.

The present invention further discloses a syrup wherein the dry base of the syrup consists of between:

7 % w/w to 52% w/w 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS),

24.5% w/w to 52% w/w 1-O-α-D-glucopyranosyl-D-mannitol (1,1 GPM),

0% w/w to 52% w/w 1-O-α-D-glucopyranosyl-D-sorbitol (1,1 GPS),

0% w/w to 1.3% w/w sorbitol (DP1),

- 2.8% w/w to 13.8% w/w maltitol (DP2),
- 1.5% w/w to 4.2% w/w maltotriitol (DP3),
- 3.0% w/w to 13.5% w/w higher polyols (DPn).

These syrups are used for the preparation of sugar-free hard candies, which are transparent, non-hygroscopic, non-cariogenic and non-sticky.

The present invention further relates to a sugar-free non-cariogenic hard candy with a mass viscosity of at least 25,000 mPa.s, and a candy surface stickiness below 180 g (50% RH, 22-23°C) and a moisture pick-up (hygroscopicity at 70% R.H and 25°C) after 14 days below 1.5%.

The current invention relates to a process for the production of a sugar-free noncariogenic hard candy comprising the following steps:

- a) preparing a syrup at dry substance between 60% to 80% consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup characterised in that the dry substance of the syrup comprises 86% w/w isomalt, preferably between 85% w/w and 79% w/w isomalt, more preferably 75% w/w isomalt, and the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols, preferably between 25% w/w and 50% w/w higher polyols,
- b) cooking at a temperature between 145°C and 170°C and low vacuum, and
- c) shaping according to stamping or deposit method.

The current invention further relates to a process wherein flavour and/or colouring matter is added during shaping.

The current invention discloses a process wherein the syrup comprises between 10 to 35% by weight water.

The current invention further relates to a process wherein the water content of the hard candy is less than 4% by weight, preferably less than 2% by weight or less, based upon the weight of the hard candy.

Non-sticky, non-hygroscopic and non-cariogenic sugar-free hard candies are obtained.

#### Brief description of the drawings

Figure 1 shows the mass viscosity profile of the hard candies prepared with C☆ Maltidex C16510, which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose

powder (C☆ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols)-△-), which is compared to the mass viscosity of hard candies prepared from hydrogenated isomaltulose (C☆ Maltidex C16500,\_\_), respectively.

Figure 2 shows the hygroscopicity (at 70% relative humidity, and 25°C) of hard candies prepared with hydrogenated isomaltulose (C☆ Maltidex C16500, -□-), hydrogenated starch hydrolysate syrup (C☆ Maltidex M16311, -o-), and (C☆ Maltidex C16510, which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C☆ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols) -△-), respectively.

Figure 3 shows the telemetric evaluation of hard candies prepared with C\$\times\$ Maltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C\$\times\$ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols) followed by sucrose intake.

#### Detailed description of the invention

The present invention discloses a syrup at dry substance between 60% to 80%, preferably at dry substance of about 70% consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup characterised in that the dry substance of the syrup comprises 86% w/w isomalt, preferably between 85% w/w and 79% w/w, more preferably 75% w/w isomalt, and the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols, preferably between 25% w/w and 50% w/w higher polyols.

The syrups can be obtained by hydrogenating mixtures of starch hydrolysates and isomaltulose or 'isomerised' saccharose, or by mixing the hydrogenated products, which

are obtained by hydrogenation of starch hydrolysate and isomaltulose and 'isomerised' saccharose, respectively, until the aforementioned composition is obtained.

Starch hydrolysates are obtained by the enzymatic or acidic hydrolysis of starch and the starch hydrolysate comprises glucose, maltose, maltotriose, and higher glucose oligomers ((DPn where n = >3). A suitable starch hydrolysate comprises between 22% w/w and 55% w/w higher oligomers, preferably between 25% w/w and 50% w/w higher oligomers.

The dry substance of a typical suitable starch hydrolysate syrup consists of:

glucose:

1 - 5% w/w

maltose:

20 - 55% w/w

maltotriose:

11-16.6% w/w

higher oligomers:

22 - 54% w/w

Isomaltulose or 6-O-α-D-glucopyranosyl-D-fructofuranose is synthesised from sucrose by the action of an enzyme present in bacterial strains like *Protaminobacter* rubrum, *Erwinia* rhapontici and *Serratia* plymuthica.

'Isomerised' saccharose is obtained by enzymatic conversion of saccharose (i.e. sucrose) into a saccharide mixture, which is containing trehalulose and isomaltulose.

Hydrogenation of the mixtures of starch hydrolysate and isomaltulose or 'isomerised saccharose results in mixtures comprising sorbitol, maltitol, maltotriitol, and hydrogenated oligomers (higher polyols), 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), and 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM), and 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS).

The components such as sorbitol, maltitol, maltotriitol, and hydrogenated oligomers (higher polyols) are obtained by the hydrogenation of starch hydrolysate syrups. The other components such as 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), and 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM), and 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS) are obtained by hydrogenation of isomaltulose and 'isomerised' saccharose.

Hydrogenation of a starch hydrolysate syrup can give a typical composition wherein the dry substance consists of 52.3 - 53.6% w/w maltitol, 3.3-3.9% w/w sorbitol,

15.6 – 16.6% w/w (maltotriitol) and 26.4-28.1% w/w higher polyols (hydrogenated oligomers), and the dry substance is 70%. Whenever the dry substance of the syrup contains at least 50% w/w DP<sub>2</sub>, the syrup is defined as a maltitol syrup.

Isomalt powder is hydrogenated isomaltulose powder and can be obtained by the hydrogenation of isomaltulose which results in a quasi-equimolar mixture of 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), and 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM). A more typical composition consists of 52.6 – 53.6% w/w 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), and 44.7 – 46.6% w/w 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM).

Isomalt syrup is hydrogenated 'isomerised saccharose' which can be prepared according to a method as is described in EP 0 625 578, and the dry substance of the syrup comprises a mixture of 10% w/w to 50% w/w 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), 35% w/w to 60% w/w 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM) and 2% w/w to 60% w/w 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS).

The dry substance of a more typical composition, obtained after the hydrogenation of 'isomerised' saccharose, comprises 43.6% w/w 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), 49.2% w/w 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM) and 3.1% w/w 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS).

The present invention discloses a syrup and the dry substance thereof is consisting of between 14% - 25% w/w hydrogenated starch hydrolysate syrup (dry substance) and between 75% - 86% w/w isomalt and it has the following composition:

7 % w/w to 52% w/w 6-O-α-D-glucopyranosyl-D-sorbitol (1,6 GPS), 24.5% w/w to 52% w/w 1-O-α-D-glucopyranosyl-D-mannitol (1,1 GPM), 0% w/w to 52% w/w 1-O-α-D-glucopyranosyl-D-sorbitol (1,1 GPS), 0% w/w to 1.3% w/w sorbitol (DP1), 2.8% w/w to 13.8% w/w maltitol (DP2),

1.5% w/w to 4.2% w/w maltotriitol (DP3),

3.0% w/w to 13.5% w/w higher polyols (DPn).

A typical composition of the current invention, i.e. C& Maltidex C16510 refers to 70/30 isomalt/hydrogenated starch hydrolysate mixture and is which is a syryp at 70% dry substance and consisting of 70% hydrogenated isomaltulose powder (C& Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols) The dry substance of C& Maltidex C16510 has the following composition:

DP<sub>1</sub>:

0.7 - 1.0 % w/w

DP<sub>2</sub>:

10 - 12% w/w

 $DP_3$ :

2.4 - 4.4% w/w

DP<sub>n</sub>:

4.6 - 6.6 % w/w

1,6 GPS:

41.5 - 42.3 % w/w

1,1 **GPM**:

35.3 - 36.8 % w/w

These syrups are used for the preparation of sugar-free hard candies, which are transparent, non-hygroscopic, non-cariogenic and non-sticky.

The current invention relates to a process for the production of a sugar-free non-cariogenic hard candy comprising the following steps:

- a) preparing a syrup at dry substance between 60% to 80% consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup characterised in that the dry substance of the syrup comprises 86% w/w isomalt, preferably between 85% w/w and 79% w/w isomalt, more preferably 75% w/w isomalt, and the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols, preferably between 25% w/w and 50% w/w higher polyols,
- b) cooking at a temperature between 145°C and 170°C and low vacuum, and
- c) shaping according to stamping or deposit method.

Production of the hard candies may be carried out in batch evaporators or in continuous cookers and the process time at elevated temperature generally being up to 15 minutes, preferably in the range 5 to 10 minutes.

The process used to produce hard candies from maltitol containing syrups customarily operates at a temperature between 145°C and 170°C, preferably between 150°C and 160°C. At these temperatures it is preferable to apply a low vacuum, suitably 0.6 to 0.8 bar at the end of the heating period to facilitate water removal. The shaping of the hard candies is performed according to either one of the classically applied methods, being the 'stamping' method and the 'depositing' method, respectively. In the 'stamping' method the cooked mass is cooled to 90°C or 100°C, and eventually colour, flavour and acid are mixed in. Then the mass is further cooled to 60°C or 70°C for shaping. After further cooling the candies are wrapped. In the 'depositing' method the cooked mass is cooled to 110°C or 120°C, and eventually colour, flavour and acid are mixed in. The hot mass is dosed in moulds, further cooled and demoulded afterwards. The current invention further relates to a process wherein flavour and/or colouring matter can be added during shaping.

After further cooling, the hard candies can be wrapped. The obtained sugar-free hard candies, which are transparent, non-hygroscopic, non-cariogenic can be loose packed in boxes due to their non-stickiness.

In each method, the heating phase is followed by a cooling phase and by applying more viscous mixtures (i.e. high mass viscosity) the workability is improved, the processing time of the cooling phase is shortened, and the final viscosity is reached sooner. In principle the processing time of the cooling phase is easily reduced with one quarter of the total time compared to the processing time required to cool the mass consisting of syrups based on hydrogenated isomaltulose alone. When working with a lab cooker on quantities of about 4 kg syrup, the cooling phase can easily be shortened with about 10 to 15 minutes compared to the cooling phase where hydrogenated isomaltulose syrups are applied solely. The processing time of the cooling phase of 4 kg syrup consisting of hydrogenated isomaltulose is about 40 to 60 minutes, while with the syrups of the current invention the processing time is shortened with 10 to 15 minutes.

The mass viscosity is measured directly after cooking with an oscillating shear-disc viscometer. The measurement is started at 135°C and the sample is cooled with constant rate of 2.8°C/ minute to 94°C and the measured values are recorded by means of a potentiometric line recorder.

The mass viscosity of hard candies prepared with hydrogenated isomaltulose is around 20,000 mPa.s at 94°C and hard candies prepared with hydrogenated isomerised saccharose have a mass viscosity of about 15,000 mPa.s. In comparison, the mass viscosity of Ct Maltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (Ct Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols)) is about 30,000 mPa.s at 94°C. This increased mass viscosity results in improved workability and the cooling time is reduced with 10 to 15 minutes when working in a lab cooker of 4 kg scale.

Applying syrups, which are obtained by the hydrogenation of starch hydrolysates and isomaltose or 'isomerised' saccharose wherein the dry substance of starch hydrolysate contains less than 22% w/w higher oligomers, results in hard candies having a mass viscosity below 25,000 mPa.s, namely about 23,600 mPa.s.

Hard candies with a mass viscosity of at least 25,000 mPa.s, preferably higher than 27,000 give good workability and significant reduction of the processing time of the cooling phase. The time to reach the appropriate viscosity before moulding, is shortened with one quarter of the total cooling time of syrups based on hydrogenated isomaltulose alone. Furthermore, by applying the syrups of the current invention not only the mass viscosity but also the plasticity of the mass is improved during processing.

The feedstock for preparing hard candies of the present invention may comprise between 10 to 35 % by weight of water based on the weight of the mixture, most often about 30% by weight water. This feedstock is heated to an elevated temperature until a product is obtained which preferably contains less than 5% by weight water, more preferably less than 4%, more preferably less than 2% by weight or less, based upon the weight of the candy.

Furthermore the polyol-containing feedstock of the present invention also may include flavour and/or colouring matter or any other additive commonly found in hard candy products.

The candy stickiness test is performed with the Texture Analyser TA-XT2 from Stable Micro Systems. The stickiness measurement can be done by storing the candy several minutes to hours at specific conditions of humidity and temperature and the more sticky the candy the higher the adhesive force becomes. The confectionery hygroscopicity is measured in a microclimate chamber with an accurate regulation system having the possibility to create conditions of temperature from 10°C to 98°C and relative humidity from 10 to 95%. The moisture pick-up of the samples placed in the microclimate chamber stored under specific conditions of temperature and humidity is calculated from the difference in weight of the samples after a specific storage time.

Hard candies prepared with hydrogenated isomaltulose give a stickiness of 175 g (after 10 minutes cooling) at 21°C and 52% relative humidity (RH), while hard candies prepared with C& Maltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C& Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols) have under similar conditions a candy surface stickiness of 171 g.

Applying syrups, which are obtained by the hydrogenation of starch hydrolysates and isomaltose or 'isomerised' saccharose wherein the dry substance of starch hydrolysate contains less than 22% w/w higher oligomers, gives hard candies with surface stickiness (21°C at 52% RH after 10 minutes cooling) of 215 g.

Stickiness of hard candies prepared from hydrogenated isomerised saccharose is determined as being 173 g at 21°C (10 minutes cooling) and 49% RH. Under the same conditions, hard candies prepared with C\$\pi\$ Maltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C\$\pi\$ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols) have a candy surface stickiness of 167g.

Surprisingly the surface stickiness of hard candies prepared with C\$\times\$ Maltidex C16510 is at least as low as the candy surface stickiness of hard candies prepared with

hydrogenated isomaltulose and is even better than surface stickiness of hard candies prepared with hydrogenated isomerised saccharose. Using syrups, which are obtained by the hydrogenation of mixtures comprising starch hydrolysate with less than 22% w/w higher oligomers, results in more sticky hard candies.

Relative humidity below 50% and 22-23°C are ideal conditions to store demoulded hard candies prepared with C\$\times\$ Maltidex C16510, (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C\$\times\$ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols). Under these conditions the candy surface stickiness should not exceed 200 g, preferably is not higher than 180 g.

The corresponding hygroscopicity (moisture pick-up) is slightly increased from 0.48% to 1.2% (after 14 days at 70% RH and 25°C) for hard candies prepared with hydrogenated isomaltulose and hard candies prepared with CAMaltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (CAMAltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols), respectively. This increase is insignificant if one considers that moisture pick-up of candies prepared with hydrogenated starch hydrolysate syrups goes up to 11%. The hygroscopicity of hard candies, which are prepared with syrups obtained by the hydrogenation of starch hydrolysates and isomaltose or 'isomerised' saccharose wherein the dry substance of starch hydrolysate contains less than 22% w/w higher oligomers, is about 1.15%. In general a moisture pick-up less than 5% after 14 days is regarded as acceptable.

Due to the low hygroscopicity of the hard candies prepared with C☆ Maltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C☆ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated

starch hydrolysate is comprising between 22% and 31% w/w higher polyols), the shelf life is correspondingly increased.

The telemetry technique is used to determine cariogenicity and continuously records plaque pH changes *in vivo* at the enamel-plaque interface and the plaque accumulates on the inserted glass electrode. If the plaque pH stays on the "alkaline side" of 5.7 within 30 minutes after consumption, the food can be labelled 'safe for teeth', or non-cariogenic. Hard candies prepared with C\$\frac{1}{2}\$ Maltidex C16510 have pH 6 in the telemetric method and are thus non-cariogenic.

The present invention results in non-hygroscopic, non-sticky, non-cariogenic hard candies with mass viscosity of at least 25,000 mPa.s, a candy surface stickiness below 180 g (50% RH, 22-23°C) and moisture pick-up (hygroscopicity at 70% R.H and 25°C) below 1.5%. Moreover as is well known the presence of maltitol improves the flavour release.

The present invention is illustrated by way of the following examples.

#### Example 1.

#### Cooking

4 kg C☆Maltidex C16510 (which is a syryp at 70% dry substance and consisting of 70/30 isomalt/hydrogenated starch hydrolysate mixture (= 70% hydrogenated isomaltulose powder (C☆ Maltidex C16500) and 30% hydrogenated starch hydrolysate syrup added at commercial base (=70% dry substance) and wherein the dry substance of hydrogenated starch hydrolysate is comprising between 22% and 31% w/w higher polyols) and the composition of dry substance is 0.7 – 1.0 % w/w sorbitol, 10 - 12% w/w maltitol, 2.4 – 4.4% w/w maltotriitol, 4.6 – 6.6 % w/w higher polyols, 41.5 – 42.3 % w/w 6-O-α-D-glucopyranosyl-D-sorbitol (1,6 GPS), 35.3 – 36.8 % w/w 1-O-α-D-glucopyranosyl-D-mannitol (1,1 GPM)) was placed in the lab cooker without water addition. It was cooked under vacuum at 155°C during 5 minutes to reach an end-moisture of max. 1.6%.

#### Shaping

"Depositing" method

The cooked mass was cooled to 110-120°C and colour, flavour and acid were mixed in. The hot mass was dosed in Teflon coated aluminium moulds and allowed cooling further, followed by demoulding. After further cooling the hard candies were wrapped.

#### Characterisation

#### a) Viscosity of Hard Candies

The oscillating shear-disc viscosimeter consists of two discs, which are vertically installed and face each other in parallel.

The shear-disc, which is arranged above the oscillating sample disc, is connected with a torque-measuring device. The lower disc is connected with the drive and it oscillates at an adjustable frequency and with a constant oscillating angle. A digital temperature control is done for both discs by means of a circulation thermostat with heating capacity up to 210°C and cooling coil with a capacity up to 20°C.

A small sample of the mass was brought directly after cooking on the shear disc, both discs were tilted together, and oscillating was started. The measurement was started at 135°C and cooled with constant rate of 2.8°C/ minute to 94°C, and the measured values were recorded by means of a potentiometric line recorder.

The results are displayed in Table 1.

#### b) Confectionery Hygroscopicity

### Microclimate Chamber

The microclimate chamber is made from a stainless steel interior, with conditioned air and diffused moisture injection microprocessor controlled. The door opening gives access to the total working space in which the samples are placed. The microprocessor achieves precise environmental control and the distinct advantage of rapid recovery after each door opening. By means of a fan and air guide walls, a forced but moderated air circulation ensures an even airflow over the samples.

The moisture pick-up of the samples placed in the microclimate chamber stored at 70% relative humidity and at 25°C was calculated from the difference in weight of the samples after 14 days.

The results are displayed in table 1.

#### c) Candy Stickiness test

The candy stickiness test is performed with the Texture Analyser TA-XT2 from Stable Micro Systems.

A moulded candy having a diameter of 40 mm and 5 mm thickness was fitted at the lower jaw of the texture analyser base. A transparent foil loop of specific dimensions (100 mm length and 12 mm width) was fitted into the upper jaw and brought on the candy surface with a force of 40 g. The loop was then pulled away from the candy surface at high speed (10 mm/sec) and the adhesive force was measured. The stickiness measurements were done at 52% relative humidity at 21°C or at 49% relative humidity and 21°C.

The results are displayed in table 1.

Table 1

	Hard candy with C☆Maltidex C16510
Mass viscosity at 94°C (mPa.s):	30,000
Hygroscopicity (70% R.H, 25°C, after 14 days)	1.2%
Stickiness (at 52% RH, 21°C)	171 g

The viscosity is shown in Figure 1.

The confectionery hygroscopicity is displayed in Figure 2.

The more sticky the candy the higher the adhesive force (here expressed in g).

The hard candies have high mass viscosity, and are non-hygroscopic and non-sticky.

#### Telemetric method

The cariogenicity of hard candies prepared with C☆Maltidex C16510 is determined with the telemetric method.

The telemetry technique continuously records plaque pH changes *in vivo* at the enamel-plaque interface and the plaque accumulates on the inserted glass electrode. If the plaque pH stays on the "alkaline side" of 5.7 within 30 minutes after consumption, the food can be labelled 'safe for teeth', or non-cariogenic.

Figure 3 shows the telemetric evaluation of hard candies prepared with C☆Maltidex C16510, followed by sucrose intake.

After consumption of hard candies prepared with C☆Maltidex C16510 pH stays above 6 and the hard candies are thus non-cariogenic.

#### Example 2.

#### Cooking

4 kg syrup (d.s. = 70% and wherein the composition of dry substance is: 0.3-0.7 % w/w sorbitol, 6.3-8.4% w/w maltitol, 1.3 – 3.4% w/w maltotriitol, 2.7 – 4.7 % w/w higher polyols, 45.2 - 46.1 % w/w 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), 38.4 – 40.1 % w/w 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM)) was placed in the lab cooker without water addition. It was cooked under vacuum at 155°C during 5 minutes to reach an end-moisture of max. 1.5%.

Shaping of the hard candies was similar as in example 1. The hard candies were characterised by measuring the mass viscosity, hygroscopicity, and stickiness according to the methods described in example 1.

The obtained results are displayed in Table 2.

Table 2

	Hard candy with syrup of example 2
Mass viscosity at 94°C (mPa.s):	25,000
Hygroscopicity (70% R.H. 25°C, after 14 days)	0.96%
Stickiness (at 52% RH, 21°C)	176 g

The hard candies have high mass viscosity, and are non-hygroscopic and non-sticky.

### Comparative example 1.

#### Cooking

4 kg hydrogenated isomaltulose powder (C\$\times\$ Maltidex C16500) was first mixed with 1.3 kg water and pre-heated to 90-100°C. Then the mixture was cooked up in the lab cooker under vacuum at 155°C during 5 minutes to reach an end-moisture of 1.6%.

Shaping of the hard candies was similar as in example 1. The hard candies were characterised by measuring the mass viscosity, hygroscopicity, and stickiness according to the methods described in example 1.

The obtained results are displayed in Table 3.

Table 3

	Hard candy with C☆Maltidex C16500
Mass viscosity at 94°C (mPa.s):	20,000
Hygroscopicity (70% R.H, 25°C, after 14 days)	0.48%
Stickiness (at 52% RH, 21°C)	175 g
Stickiness (at 49% RH, 21°C)	167 g

The hard candies are non-hygroscopic, non-sticky but the mass viscosity is too low.

#### Comparative Example 2.

#### Cooking

4 kg hydrogenated starch hydrolysate syrup at 70% dry substance (C☆ Maltidex L16303, M16311 or H16323) was placed in the lab cooker without water addition. It was cooked under vacuum at 168°C during 5 minutes to reach an end-moisture of max. 1%.

Shaping of the hard candies was similar as in example 1. The hard candies were characterised by measuring the mass viscosity, hygroscopicity, and stickiness according to the methods described in example 1.

The obtained results are displayed in Table 4.

Table 4

	Hard candy with hydrogenated starch
	hydrolysate syrup
Mass viscosity at 94°C (mPa.s):	533,029
Hygroscopicity (70% R.H, 25°C, after 14 days)	11%

The hard candies are very hygroscopic.

#### Comparative Example 3.

#### Cooking

4 kg isomalt/hydrogenated starch hydrolysate syrup wherein the dry substance comprises below 22% w/w higher polyols (d.s. = 70% and dry substance consists of between 41.5-42.3% w/w 6-O-α-D-glucopyranosyl-D-sorbitol (1,6 GPS), between 35.3 – 36.8% w/w 1-O-α-D-glucopyranosyl-D-mannitol (1,1 GPM), between 0.8 – 1.0% w/w sorbitol, between 10.5 – 12.5% w/w maltitol, between 3.3 – 5.3% w/w maltotriitol, and between 3.1 – 5.1% w/w higher polyols) was placed in the lab cooker without water addition. It was cooked under vacuum at 155°C during 5 minutes to reach an end-moisture of max. 1.6%.

Shaping of the hard candies was similar as in example 1. The hard candies were characterised by measuring the mass viscosity, hygroscopicity, and stickiness according to the methods described in example 1.

The obtained results are displayed in Table 5.

Table 5

	Hard candy with syrup of comparative					
	example 3					
Mass viscosity at 94°C (mPa.s):	23,600					
Hygroscopicity (70% R.H. 25°C, after 14 days)	1.15%					
Stickiness (at 52% RH, 21°C)	215 g					

The hard candies are non-hygroscopic, but sticky and the mass viscosity is too low.

#### Comparative Example 4.

#### Cooking

4 kg hydrogenated isomerised saccharose syrup (d.s. = 70% and dry substance comprises 43.6% 6-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,6 GPS), 49.2% 1-O- $\alpha$ -D-glucopyranosyl-D-mannitol (1,1 GPM) and 3.1% 1-O- $\alpha$ -D-glucopyranosyl-D-sorbitol (1,1 GPS)) was placed in the lab cooker without water addition. It was cooked under vacuum at 155°C during 5 minutes to reach an end-moisture of max. 1.6%.

Shaping of the hard candies was similar as in example 1. The hard candies were characterised by measuring the mass viscosity, hygroscopicity, and stickiness according to the methods described in example 1.

The obtained results are displayed in Table 6.

## Table 6

	Hard candy with hydrogenated					
	'isomerised' saccharose					
Mass viscosity at 94°C (mPa.s):	15,000					
Hygroscopicity (70% R.H, 25°C, after 11 days)	0.96%					
Stickiness (at 49% RH, 21°C)	173 g					

The hard candies are non-hygroscopic, non-sticky, but the mass viscosity is too low.

#### Claims

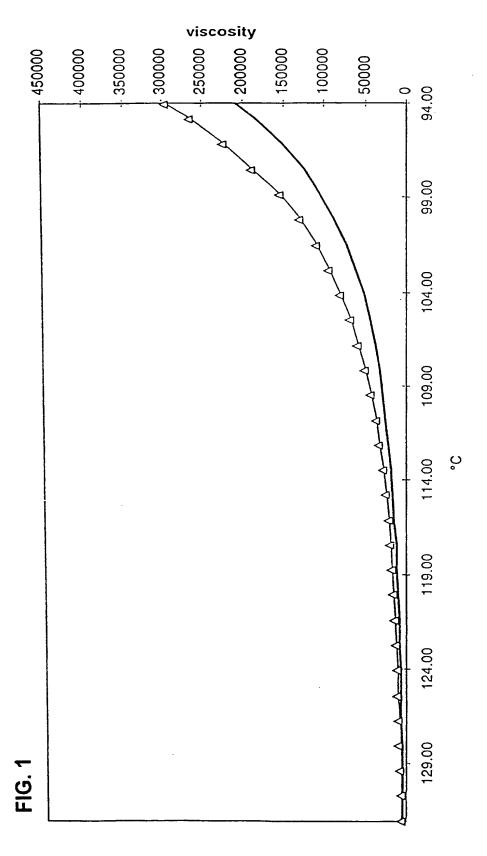
- 1. A syrup at dry substance between 60% to 80%, preferably at dry substance of about 70% consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or isomalt syrup characterised in that the dry substance of the syrup comprises 86% w/w isomalt, preferably between 85% w/w and 79% w/w isomalt, more preferably 75% w/w isomalt, and the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols, preferably between 25% w/w and 50% w/w higher polyols.
- 2. A syrup according to claim 1 characterised in that the dry base of the syrup consists of between:

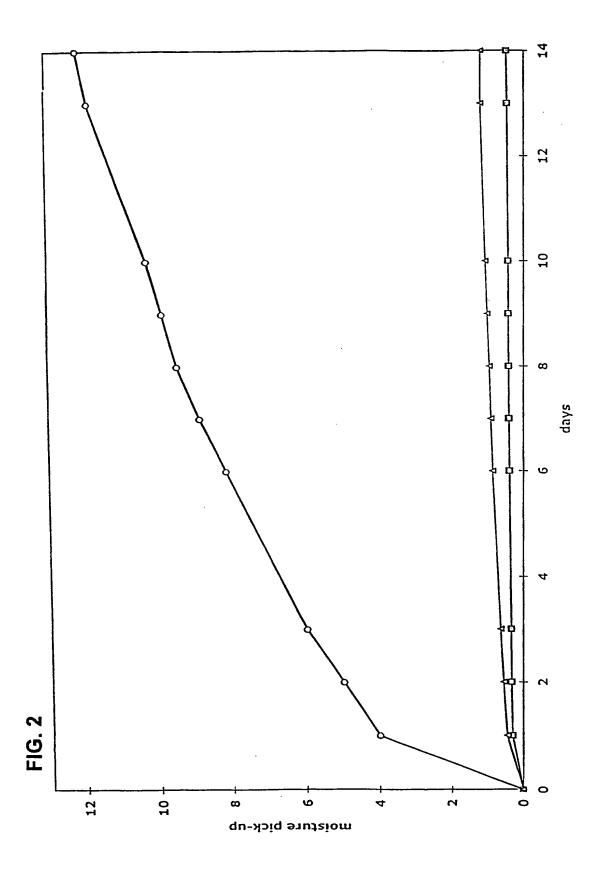
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7 % w/w to 52% w/w 6-O-\alpha-D-glucopyranosyl-D-sorbitol (1,6 GPS), 24.5% w/w to 52% w/w 1-O-\alpha-D-glucopyranosyl-D-mannitol (1,1 GPM), 0% w/w to 52% w/w 1-O-\alpha-D-glucopyranosyl-D-sorbitol (1,1 GPS), 0% w/w to 1.3% w/w sorbitol (DP<sub>1</sub>), 2.8% w/w to 13.8% w/w maltitol (DP<sub>2</sub>), 1.5% w/w to 4.2% w/w maltotriitol (DP<sub>3</sub>), 3.0% w/w to 13.5% w/w higher polyols (DP<sub>n</sub>).
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- 3. A sugar-free non-cariogenic hard candy comprising a syrup according to claim 1 or 2.
- 4. A sugar-free non-cariogenic hard candy according to claim 3 characterised in that the mass viscosity is at least 25,000 mPa.s, and that the candy surface stickiness is below 180 g (50% RH, 22-23°C) and the moisture pick-up (hygroscopicity at 70% R.H and 25°C) after 14 days is below 1.5%.
- 5. A process for the production of a sugar-free non-cariogenic hard candy comprising the following steps:
  - a) preparing a syrup at dry substance between 60% to 80% consisting of a mixture of hydrogenated starch hydrolysate syrup and isomalt powder or

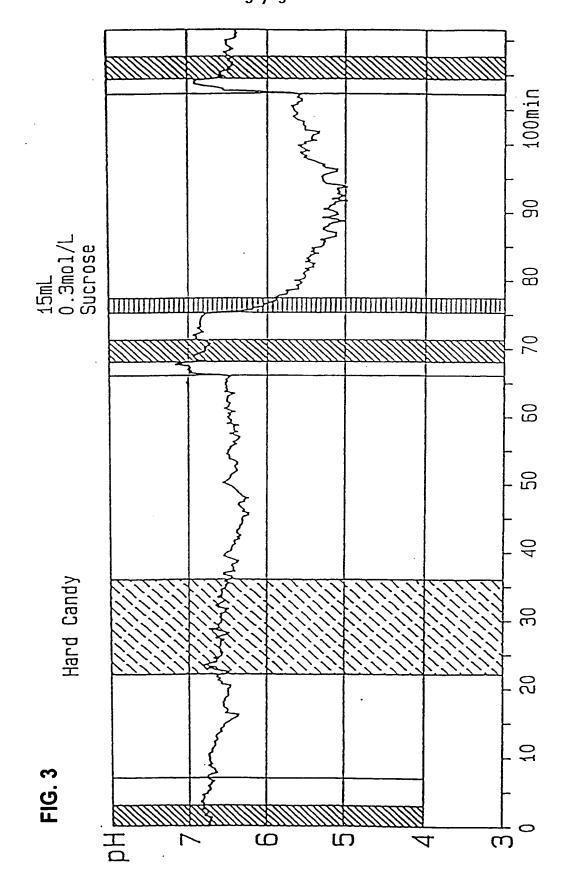
isomalt syrup characterised in that the dry substance of the syrup comprises 86% w/w isomalt, preferably between 85% w/w and 79% w/w isomalt, more preferably 75% w/w isomalt, and the dry substance of the hydrogenated starch hydrolysate syrup comprises between 22% w/w and 55% w/w higher polyols, preferably between 25% w/w and 50% w/w higher polyols,

- b) cooking at a temperature between 145°C and 170°C and low vacuum, and
- c) shaping according to stamping or deposit method.
- 6. A process according to claim 5 characterised in that flavour and/or colouring matter is added during shaping.
- 7. A process according to claim 5 or 6 characterised in that the syrup comprises between 10 to 35% by weight water.
- 8. A process according to anyone of claims 5 to 7 characterised in that the water content of the hard candy is less than 4% by weight, preferably less than 2% by weight or less, based upon the weight of the hard candy.





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## SUBSTITUTE SHEET (RULE 26)



nal Application No

PCT/EP 00/06016 A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A23G3/00 A23G A23G3/02 A23G3/30 A23L1/236 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) A23G A23L IPC 7 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, FSTA C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Category ° 1,5-8Y FRITZSCHING, B.: "Isomalt in hard candy applications." MANUFACTURING CONFECTIONER., vol. 75, no. 11, 1995, pages 65-73, XP000862872 CHICAGO, IL., US ISSN: 0163-4364 cited in the application page 67, column 2 -column 3 page 69, column 1 page 70, column 1 -page 71, column 3; figure 7 figure 8 Patent family members are listed in annex. Further documents are listed in the continuation of box C. X Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but "A" document defining the general state of the art which is not cited to understand the principle or theory underlying the considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention citation or other special reason (as specified) cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled other means "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 17/11/2000 9 November 2000 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 Canapagai Faten Office, P.B. 5818 Patentla: NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016

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Heezius, A

Intern Pal Application No PCT/EP 00/06016

ategory °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
•	RALEIGH W: "HSH as a bulking agent in confections."  MANUFACTURING CONFECTIONER.,  vol. 75, no. 11, 1995, pages 57-59,  XP000957699  CHICAGO, IL., US  ISSN: 0163-4364  page 57, right-hand column, paragraph 3  -page 58, right-hand column, paragraph 2  page 58, right-hand column, paragraph 2  -page 59, left-hand column, paragraph 4;  figure 3	1,5~8	
Ą	DE 42 28 278 A (SIGRIST, E.) 20 January 1994 (1994-01-20) cited in the application column 1, line 66 -column 2, line 28; claims 1-3	1,3	
A	EP 0 788 744 A (LOTTE CO. LTD) 13 August 1997 (1997-08-13) cited in the application page 3, line 25 - line 31; claims 9-11; example 8	1,3	
A	EP 0 500 977 A (ZOSTER, S.A.) 2 September 1992 (1992-09-02) cited in the application example 4	1,3	
A	US 5 578 339 A (KUNZ ET AL.) 26 November 1996 (1996-11-26) claims 1-6,21,22	1,3	
A	HÖRLEIN L.: "Production of low-calorie strawberry jam pleasant in taste and suitable for diabetics using both acesulfame-K and aspartame."  INDUSTRIELLE OBST- UND GEMUESEVERWERTUNG, vol. 80, no. 1, 1995, page 2-7 XP000863024 WOLFSBURG, DE ISSN: 0367-939X page 3, column 1	1,3	
A	EP 0 390 299 A (TOWA CHEMICAL INDUSTRY CO. LTD.) 3 October 1990 (1990-10-03) page 3, line 31 - line 40 page 3, line 52 - line 53	1,3	
A	EP 0 504 924 A (HOECHST AKTIENGESELLSCHAFT) 23 September 1992 (1992-09-23) column 2, line 15 - line 28; claims 1-4,8,10	1-9	



....urmation on patent family members

Intern: al Application No PCT/EP 00/06016

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
DE 4228278	A	20-01-1994	CH FR NL	684148 A 2693631 A 9301254 A	29-07-1994 21-01-1994 16-02-1994
EP 788744	A	13-08-1997	JP AU BR CA CZ HU NZ PL RU US	9252723 A 1019297 A 9700121 A 2195350 A 9700153 A 9700164 A 314082 A 318004 A 2142711 C 5711982 A	30-09-1997 24-07-1997 22-09-1998 19-07-1997 13-08-1997 28-10-1997 26-05-1997 21-07-1997 20-12-1999 27-01-1998
EP 500977	Α	02-09-1992	DE DE US	69111050 D 69111050 T 5300309 A	10-08-1995 23-11-1995 05-04-1994
US 5578339	А	26-11-1996	AT AU DE DE DK EP ES GR IL JP	140032 T 666073 B 6194094 A 9321600 U 59303142 D 625578 T 0625578 A 2089691 T 3020742 T 109569 A 7051079 A	15-07-1996 25-01-1996 10-11-1994 06-04-2000 08-08-1996 11-11-1996 23-11-1994 01-10-1996 30-11-1996 10-03-1998 28-02-1995
EP 390299	A	03-10-1990	AT DE DE JP JP	91389 T 69002177 D 69002177 T 2257848 A 2000078954 A	15-07-1993 19-08-1993 28-10-1993 18-10-1990 21-03-2000
EP 504924	A	23-09-1992	CA JP	2063645 A 5262782 A	23-09-1992 12-10-1993